

The curl, or waviness, placed in synthetic fibers by chemical or mechanical action is called crimp. It is of great importance in the processability of staple fibers. Crimp is also introduced in some cases, into continuous-filament yarns to alter their appearance and feel, e.g., in nylon carpet yarn. Cotton and wool possess natural crimp.

Denier is a measure of the weight of fibers per unit length and is defined as the weight in grams of 9000 m. Another unit is the *tex* which is the weight of 1000 m.

The first synthetic fibers were circular, but special characteristics can be imparted by manufacturing fibers with nonround cross sections. A carpet yarn, developed in Germany,^{1a} has a pentagonal cross section and contains six structural holes. As light passes through the holes it is deflected and broken up and thus reduces the visibility of soil particles. The five-sided fibers also aid in soil release. Most of the fibers on the market today have filaments whose cross sections are not uniformly round.

SYNTHETIC FIBERS

CLASSIFICATION. The versatile noncellulosic fibers, whose market is rapidly growing, are classified chemically and by the method of spinning in Table 35.1. The manufacture of all true synthetic fibers begins with the preparation of a polymer consisting of very long, chain-like molecules. The polymer is spun and this results, in most cases, in a weak, practically useless fiber until it is stretched to orient the molecules and set up crystalline lattices. By controlling, within limits, the degree of orientation, crystallinity, and average chain length, a single polymer can be used to make a number of fibers with widely differing mechanical properties ranging from weak and stretchy to strong and stiff. Two elements important in determining the range of the polymer's mechanical properties are the attractive forces between the molecules and the flexibility and length of the molecular chains.

Spinning procedures are divided into melt, dry, and wet.

1. Melt spinning, developed for nylon and also used for polyester, polyvinyl, polypropylene, and others, involves pumping molten polymer through capillaries or spinnerets. The polymer streams that emerge from the spinneret openings are solidified by quenching in cool air.

2. In dry spinning, the polymer is dissolved in a suitable organic solvent. The solution is forced through spinnerets, and upon evaporation of the solvent in warm air, dry filaments are formed. Some acrylics and vinyl-acrylic copolymers are spun in this manner.

3. Wet spinning involves spinning of a solution of polymer and coagulation of the fiber in a chemical bath. As an example, a polymer dissolved in dimethyl acetamide could be coagulated in a bath of glycerol at 140°C, or coagulated in a bath of 40% calcium chloride at 90°C. Acrylics, such as Acrilan and Creslan, are prepared by wet spinning.

Table 35.1 gives the method of spinning for some representative fibers.

Polyamides

Nylon 6,6 was the first all-synthetic fiber made commercially and opened up the entire field. In 1981 the U.S. production was 1.18×10^6 t, of which 59 percent was used for home furnishings, mostly carpets. Apparel accounted for 20 percent and tire cord for 11 percent.

^{1a}Text. Ind. 146 (9) 106 (1982).

Table 35.1 Representative Synthetic Fibers and Films*

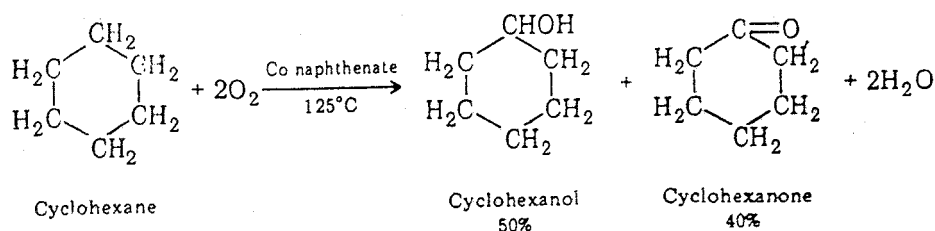
Classification	Spinning†
<i>Polyfibers and Films</i>	
Polyamides, or nylon, fibers	Melt
Nylon 66, nylon 6, Qiana	
Polyesters	Melt
Fibers: Dacron, Trevira, Kodel, Fortrel	Melt
Films: Mylar, Cronar, Kodar, Estar	Melt
Acrylics and modacrylics	
Orlon fiber	Dry
Acrilan fiber	Wet
Creslan fiber	Wet
Dynel fiber (vinyl-acrylic)	Dry
Verel fiber	Dry
Vinyls and Vinylidines	
Saran fiber and film	Melt
Vinyon N fiber†	Dry
Spandex	
Lycra	Dry
Numa	Wet
Glospan	Wet
Olefins	
Polyethylene films	Melt
Polypropylene fibers and films: Avisun, Herculon	Melt
<i>Glass Fibers</i>	
Fiberglass	Melt
<i>Cellulosic Fibers and Films</i>	
Regenerated cellulose	
Fibers: Rayon (viscose), cuprammonium	Wet
Film: Cellophane	Wet
Cellulose esters	
Acetate fibers and films: Acele, Estron	Dry
Triacetate fiber: Arnel	Dry

*Completely synthetic or semisynthetic (cellulosics). †Classified as melt, dry, or wet.
 ‡60% vinyl and 40% acrylonitrile.

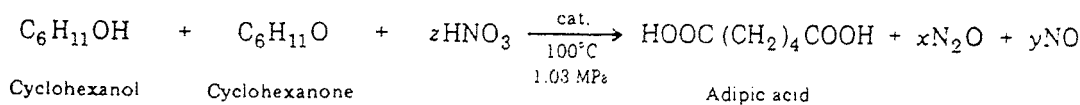
The product resulting from the polymerization reaction of adipic acid and hexamethylene diamine is called nylon 6,6 because each of the raw material chains contain six carbon atoms. Nylon 6 is the homopolymer of caprolactam, and the newly developed aramid fiber, Kevlar is an aromatic polyamide, poly-*p*-phenylene terephthalamide.

INTERMEDIATES

1. *Adipic acid.*² Adipic acid is prepared by a two-step air oxidation of cyclohexane.

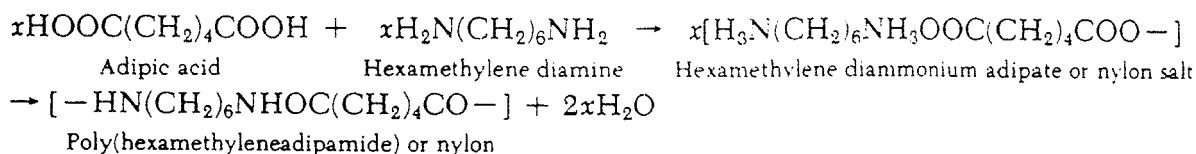


²Austin, The Industrial Significant Organic Chemicals, *Chem. Eng.* 81 (2) 131 (1974)
 Danly and Campbell, ECT, 3d ed., vol. 1, 1978, pp. 510-531.



2. **Hexamethylene diamine.**³ This compound is made from butadiene or acrylonitrile.

POLYMERIZATION AND FIBER PRODUCTION.⁴ The reaction between adipic acid and hexamethylene diamine produces hexamethylene diammonium adipate, commonly called "nylon salt." It is essential that the two intermediates be used in equimolar proportions if high fiber-forming quality polymer is to be produced. Forming the salt assures the correctly balanced proportions. It is also necessary that the material to be polymerized contain very few impurities if high-quality fibers are to be made. This is achieved by recrystallizing the nylon salt before polymerization. Figure 35.2 shows various routes to nylons. The flowchart for nylon yarn, using a batch process, is given in Fig. 35.3.



³ECT, 3d ed., vol. 1, 1978, pp. 510-531.

⁴Chapman, *Fibres*, Butterworths, London, 1974.

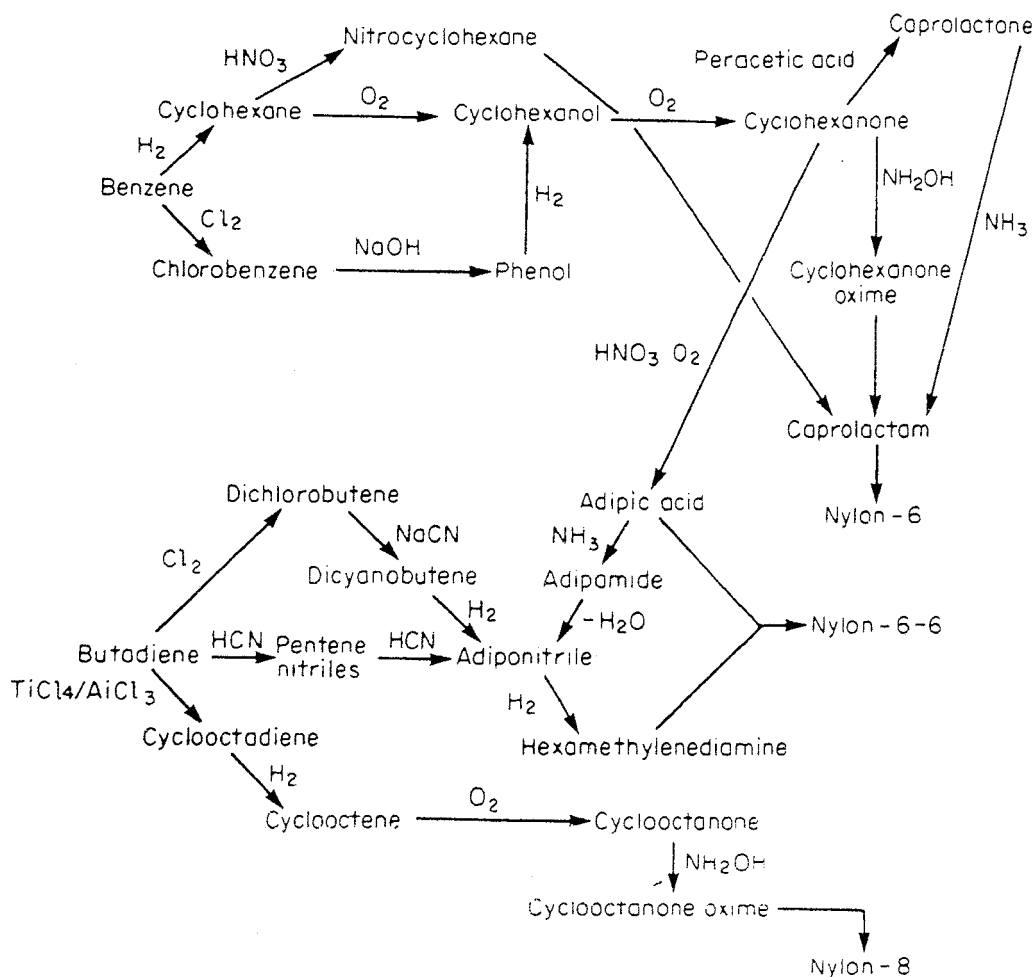


Fig. 35.2. Various routes to nylon. (Adapted from Marshall Sittig.)

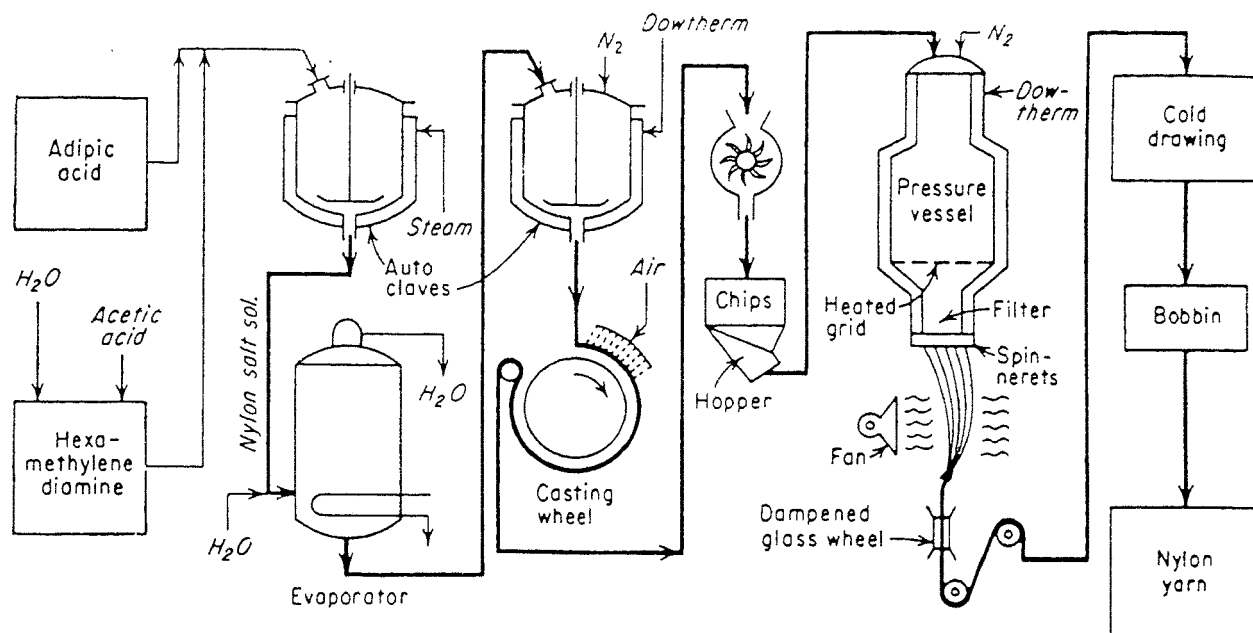


Fig. 35.3. Flowchart for nylon yarn.

The aqueous nylon salt starts on the top level of the factory, and the materials move down by gravity through the various steps. The hexamethylene diammonium adipate solution is pumped to the top level into evaporators and concentrated. Acetic acid is added to the evaporator charge to stabilize the chain length. After evaporation, the salt solution flows into jacketed autoclaves equipped with internal coils and heated by Dowtherm vapor (Fig. 35.4). Here the rest of the water is removed. TiO_2 dispersion is added, and polymerization takes place.

After polymerization is completed, the molten viscous polymer is forced out of the bottom onto a casting wheel by specially purified nitrogen at 175 to 345 kPa. Each 900-kg batch is extruded as rapidly as possible to minimize differences due to thermal treatment of the polymer. A ribbon of polymer about 30 cm wide and 6 mm thick flows on the 1.8-m casting drum. Water sprays on the inside cool and harden the underside of the ribbon; the outer is cooled by air and water. The ribbons are cut into small chips, or flakes, before being blended. Two or more batches are mixed to improve the uniformity of the feed to the spinning machine. The blenders empty into hoppers on a monorail which supply the spinning area.

A typical spinning unit is composed of a metal vessel surrounded by a Dowtherm vapor-heated jacket which keeps the temperature of the vessel above the melting point (263°C) of the nylon. Special precautions are taken to keep the spinning oxygen-free. As the nylon flake enters the vessel it strikes a grid, where it melts and flows through to the melt chamber below. Screw melters, in place of grids, may also be used to melt the flake. The molten polymer passes through the portholes in this chamber to the gear spinning pumps. They deliver it to a sand filter, which is followed by screens and a spinneret plate. The filaments are solidified by air in a cooling chimney and passed in a bundle through a steam-humidifying chamber, where the moisture content is brought to equilibrium in order to stabilize the length of the spun polymer. This is not a problem after stretching or drawing.

After lubrication on a finish roll, the yarn is stretched or drawn to the desired degree by passing it through a differential speed roller system. Here the strength or elasticity characteristics of nylon are developed, because the molecules are oriented from their previous comparatively random oriented arrangement. Stretching may be from three- to sixfold, depending on the mechanical properties desired, being stronger when the orientation by stretching is greatest. The nylon filament is then shipped to various manufacturers for processing.

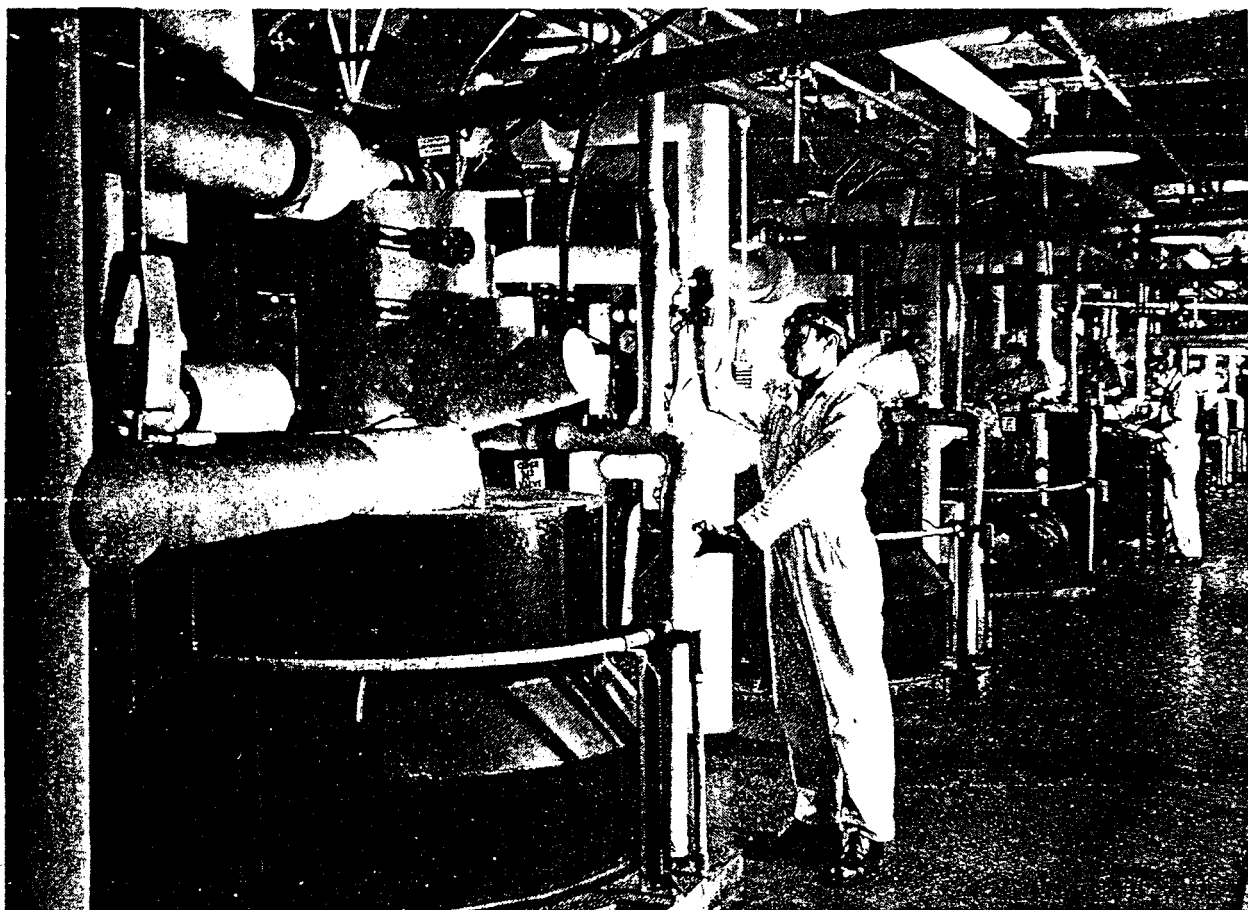


Fig. 35.4. Autoclave in DuPont nylon plant. In these receptacles polymerization takes place to form nylon polymers.

Continuous processing is more economical for larger production items. Here the pressure and temperature of the autoclave cycles are reproduced in a series of pipes and vessels. The continuous process favors uniformity of large-scale product, whereas the batch process favors flexibility among several products.

Like all other synthetic fibers that have become competitively popular, nylon in both the filament and staple form must have certain properties that are superior to natural fibers. It is stronger than *any* natural fiber and has a wet strength of 80 to 90 percent of its dry strength. Its good flexing tenacity makes it very desirable for women's hosiery, and it has good stretch recovery. Nylon's high tenacity has made it important in parachute fabrics and related non-apparel items. Nylon can be dyed by all acid and dispersed dyes. It has a low affinity for direct cotton, sulfur, and vat dyes.

Nylon 6,⁵ or nylon caprolactam, is a polymeric fiber derived from only one constituent,

caprolactam (Fig. 35.2), $\text{HN}-(\text{CH}_2)_5\text{CO}$ giving the polymer $[-(\text{CH}_2)_5\text{CO}-\text{NH}-]_n$. It has a lower melting point than nylon 6,6, but it is superior to it in resistance to light degradation, dyeability, elastic recovery, fatigue resistance, and thermal stability. Caprolactam may be made from cyclohexanoneoxime, which is obtained by treating cyclohexanone with hydroxylamine. The more modern process starts with toluene, which is oxidized to benzoic acid,

⁵Moncrieff, *Man-made Fibres*, 6th ed., Wiley, New York, 1975; Chapman, op. cit.

⁶Caprolactam, *Chem. Eng.* 81 (15) 70 (1974); The DSM Phosphate Caprolactam Process, *CHEMTECH* 7 (5) 309 (1977); *Chem. Week* 126 (21) 47 (1980).

hydrogenated to cyclohexane carboxylic acid, and then treated with nitrosyl sulfuric acid to produce caprolactam.⁶

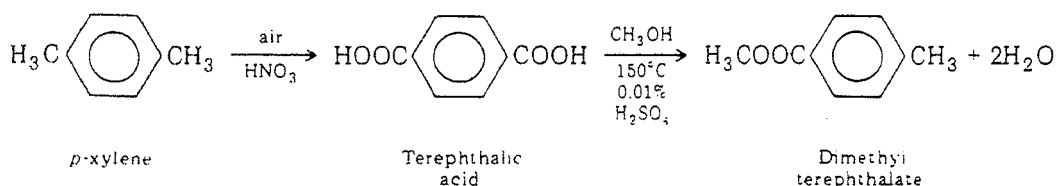
Other nylons have been prepared and have some interesting properties. Copolymers of nylon 6 and nylon 6,6 have improved properties over either polymer alone. These copolymers are used primarily for engineering resins and not for fibers.

Aromatic polyamides (aramids)⁷ have at least 85 percent of the amide linkages attached directly to two aromatic rings. The first commercial aramid was Nomex which was prepared by reacting *m*-phenylene diamine with isophthaloyl chloride to produce poly-(*m*-phenyleneisophthalamide). Kevlar is prepared similarly, but it is the para isomer and is produced from *p*-phenylenediamine and terephthaloyl chloride. The meta isomers produce polymers that are heat and flame resistant, and the para isomers produce high strength and high modulus of elasticity. Nomex is used for electrical insulating paper, protective clothing, and in space applications. Kevlar possesses ultrahigh strength and is used as a tire cord. When it is produced as a very short fiber, called Kevlar Pulp, it is used as a replacement for asbestos.

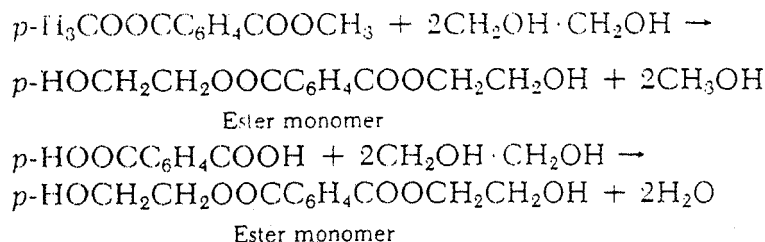
Polyesters

The common polyester fibers are polymers of the ester formed from dimethyl terephthalate and ethylene glycol.

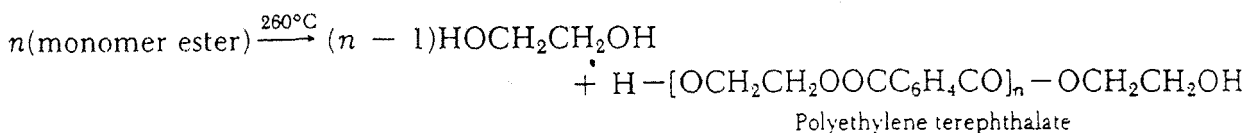
INTERMEDIATES. Dimethyl terephthalate⁸ is prepared by oxidation of *p*-xylene and subsequent esterification with methyl alcohol.



POLYMERIZATION AND FIBER PRODUCTION. Polymerization is a two-stage process in which the monomer is first prepared either by an ester interchange between dimethyl terephthalate and ethylene glycol, or by direct esterification of terephthalic acid.



The second stage is the polymerization of the monomer



⁷ECT, 3d ed., vol. 3, 1978, p. 213; *Chem. Week* 127 (22) 20 (1980); *Chem. Week* 132 (8) 43 (1983).

⁸Austin, *Chem. Eng.* 81 (22) 114 (1974).

The polymer is extruded from the bottom of the polymerizer through a slot or holes on to the surface of a water-cooled drum. The ribbon is cut to chips and dried before melt spinning in a manner similar to that described for nylon. The polymer chain contains approximately 80 benzene rings. Figure 35.5 shows the flowchart for the entire process. The filaments are stretched, with the application of heat, to about three to six times their original length.

Table 35.2 shows some of the properties of polyester fiber. It is particularly well suited for blending with wool and cotton to yield good esthetics in woven fabrics, such as men's summer suits, men's shirts, and women's dresses and blouses, and is used alone in knitted fabrics and some woven fabrics. Because of its strength it is important in the tire-cord and cordage fields. It is also used for sewing thread, fire hose, and V-belts. It is not used for women's stockings because its elastic modulus is too high, and thus it does not recover rapidly after stretching. In staple form it is employed as stuffing for pillows, sleeping bags, and comforters. Its production in 1981 was almost 1.9×10^6 t.

Acrylics and Modacrylics

Polyacrylonitrile ($-\text{CH}_2\text{CHCN}-$)_n is the major component of several industrial textile fibers, but DuPont's Orlon was the first to attain commercial-scale operation. Dyeable acrylics are generally copolymers with modifying constituents.

Orlon is made by polymerizing acrylonitrile. The ivory-white polymer is dissolved in an organic solvent, generally dimethylformamide, although it can be dissolved in many concentrated solutions of salts, like lithium bromide or more successfully in other organic solvents.

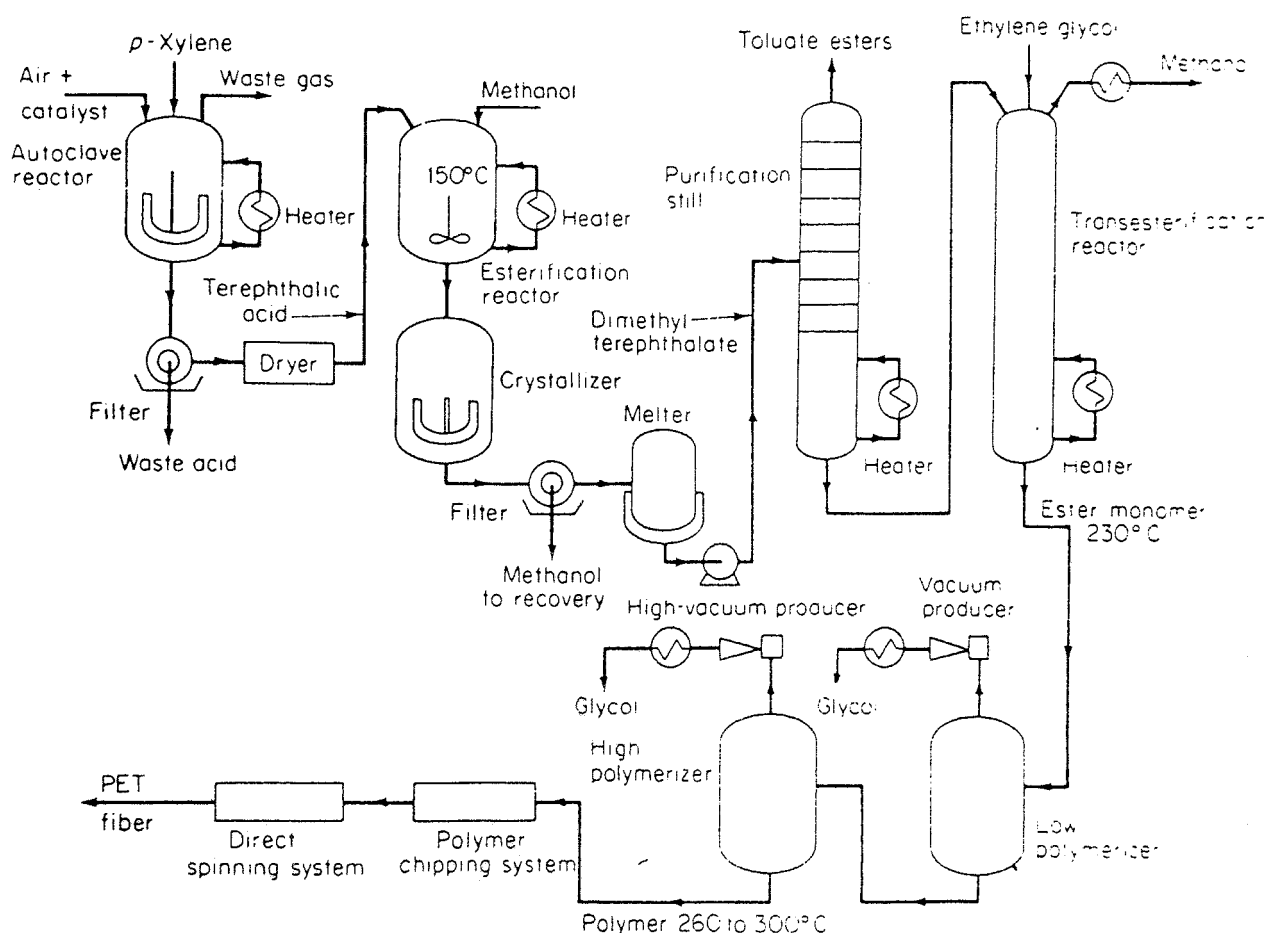


Fig. 35.5. Flowchart for the manufacture of polyester fibers.

Table 35.2 Comparison of Selected Synthetic Fibers

Fiber	Wool	Acrylic	Modacrylic	Polyesters	Nylon
Tensile strength, g./denier	1.0-1.7	4.0-5.0	3.0	4.4-6.6	4.7-5.6
Elongation, %	25-35	16-21	16	18-22	25-28
Elastic recovery	0.99 at 2%	0.97 at 2%	0.80 at 2%	90-110 at 4%	100 at 8%
Strength, mPa	137-200	405-508	302-453	536-797	467-556
Stiffness, g./denier*	3.9	24	30	23-63	20
Abrasion resistance†	90	330	—	1570	2520
Water absorbency†	21.9% at 90 RH	2% at 95 RH	—	0.5% at 95 RH	8% at 95 RH
Effect of heat	Becomes harsh 100°C, decomposes at 130°C	Sticking point 235°C	Sticking point 235°C	Sticking point 240°C	Melts 263°C
Effect of age	Little	Little	Little	Little	Slight
Effect of sun	Weakened	Very resistant	Slight	Little	Weakened
Effect of acids (concentrated, room temp.)	Resistant	Resistant	Resistant	Resistant	Weakened
Effect of alkalies	Susceptible	Partly resistant	Resistant	Resistant	Resistant
Effect of organic solvents	Resistant	Resistant	Resistant	Resistant	Resistant
Dyeability	Good	Good	Good	Difficult	Good
Resistance to moths	None	Wholly	Wholly	Wholly	Wholly
Resistance to mildew	Good	Wholly	Wholly	Wholly	Wholly

* Crease resistance: † Wet flex test, number of flexes. † RH, Relative humidity; sources: Wool vs. Synthetics, *Chem. Week* 69 (3) 11 (1951); Moncrief, *Man-Made Fibers*, 6th ed., Wiley, New York, 1975.

such as dimethoxyacetamide and tetramethylene cyclic sulfone. The solution is filtered and then dry-spun, utilizing the same spinning technique long used for acetate, namely, in solution through spinnerets, with the solvent evaporated to furnish the dry fiber. Unlike nylon which is drawn at room temperature, acrylics, like polyester, are drawn at elevated temperatures in a special machine. The fibers are stretched to three to eight times their original length to orient the molecules into long parallel chains for final strength. The staple fiber has esthetic properties like those of wool. The acrylics' resistance to chemical attack, and especially to weathering, makes them highly useful in several fields. Other acrylics, like Acrilan and Creslan, are spun wet into a coagulating bath. The end uses for acrylic fibers comprise sweaters, women's coats, men's winter suiting, carpets, and blankets. Blends with wool and other synthetics are common in some end uses. Acrylics are also suitable for pile fabrics and filter cloth.

MODACRYLIC FIBERS (MODIFIED ACRYLICS). This is a generic name for synthetic fibers in which the fiber-forming substance is any long-chain synthetic polymer composed of less than 85% but at least 35% by weight of acrylonitrile units (Federal Trade Commission).

Dynel is the name given by Union Carbide to their staple copolymer modacrylic fiber made from a resin of 40% acrylonitrile and 60% vinyl chloride. The resin is converted into staple in a continuous wet-spinning process (cf. viscose rayon). The white resin powder is dissolved in acetone, filtered, and run through a spinneret, where the fibers are formed in an aqueous spinning bath. The fiber is dried, cut, and crimped. Dynel is similar to wool in many respects and has some superior characteristics. It is used for work clothing, water-softener bags, dye nets, filter cloth, blankets, draperies, sweaters, pile fabrics, etc.

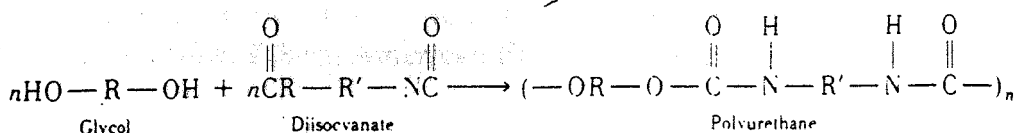
Vinyls and Vinylidines

Saran is the copolymer of vinyl chloride and vinylidene chloride. It is prepared by mixing the two monomers with a catalyst and heating. Color is added by introducing pigment into the mass. The copolymer is heated, extruded at 180°C, air-cooled, and stretched. Saran is resistant to mildew, bacterial, and insect attack, which makes it suitable for insect screens. Its chemical resistance makes it advantageous for filter-cloth applications; however, its widest use has been for automobile seat covers and home upholstery. Much film is made from Saran.

Vinyon is the trade name given to copolymers of 90% vinyl chloride and 10% vinyl acetate. The copolymer is dissolved in acetone to 22% solids and filtered, and the fibers are extruded by the dry-spinning technique. After standing, the fibers are wet-twisted and stretched. Resistance to acids and alkalis, sunlight, and aging makes Vinyon useful in heat-sealing fabrics, work clothing, filter cloths, and other related applications.

Spandex

Spandex, a generic name, is defined by the Federal Trade Commission as "a manufactured fiber in which the fiber-forming substance is a long chain synthetic polymer comprising at least 85% of a segmented polyurethane." Trade examples of these are Lycra, Glospan, and Numa fibers. Lycra, DuPont's spandex fiber, results from the following reaction:



The segmented polyurethane structure is achieved by reacting diisocyanates with long chain glycols which are usually polyesters or polyethers of 1000 to 2000 molecular weight range. The product is then chain-extended or coupled through the use of glycol, a diamine, or perhaps water. This gives the final polymer, which is converted into fibers by dry spinning. In the finished fiber the chains are randomly oriented and, when stretched, the chains become oriented but exhibit spontaneous recovery to the disordered state upon release of the force. This fiber is used in foundation garments, hose, swimwear, surgical hose, and other elastic products, sometimes in conjunction with other fibers, such as acrylic, polyester, acetate, rayon, or natural fibers, which are wrapped around a core of the elastic spandex fiber.

Polyolefins

Polyolefin fibers are usually made of polyethylene and polypropylene. They excel in special cases, such as ropes, laundry nets, carpets, blankets, and backing for tufted carpets, but are difficult to dye and their melting point is low. In 1981 the annual consumption in the United States was 292,000 t. See Chap. 34 for the preparation of the polymer.

The polymer is spun from a melt at about 100°C above the melting point because the viscosity of the molten polymer at or near the melting point is very high.

Fluorocarbons

Teflon is polytetrafluoroethylene [$-(C_2F_4)-_n$] (Chap. 20) and as fiber or film is nonflammable and highly resistant to oxidation and the action of chemicals, including strong acids, alkalis, and oxidizing agents. It retains these useful properties at high temperatures (230 to 290°C) and is strong and tough. A very important property is its low friction, leading, with its chemical inertness, to wide use in pump packings and shaft bearings.

Glass Fibers

Fiberglass wearing materials were prepared as early as 1893, when a dress of fibers about five times the diameter of the present-day product was made by Owens. Since that time, however, numerous improvements have been discovered, until at present continuous fibers as small as 5 μm in diameter are possible. The largest and original (1938) manufacturer of glass fibers is the Owens-Corning Fiberglas Corp., which markets its product under the trade name Fiberglas. Production of textile fibers in 1981 was 472,000 t. Glass fibers are derived by two fundamental spinning processes: blowing (glass wool) and drawing (glass textile fiber), as outlined in Fig. 35.6. Textile fibers⁹ can be made as continuous filaments or staple fibers and are manufactured from borosilicate glasses composed of 55% silica, and substantial amounts of alumina, alkaline earths for fluxing, and borates (Table 35.3). The low strong-alkali level reduces susceptibility to corrosion. Glass for textiles must be equal in purity to the better grades of optical glass and, when molten, must be free of any seeds or bubbles that would tend to break the continuity of the fiber.

In the continuous-filament process, specially prepared and inspected glass marbles are melted, or a batch of highly purified molten glass is allowed to flow through a set of small

⁹Carpet of Glass, *Text. Ind.* 139 (1) 40 (1975); Lowenstein, *The Manufacturing Technology of Continuous Glass Fibers*, American Elsevier, New York, 1973.

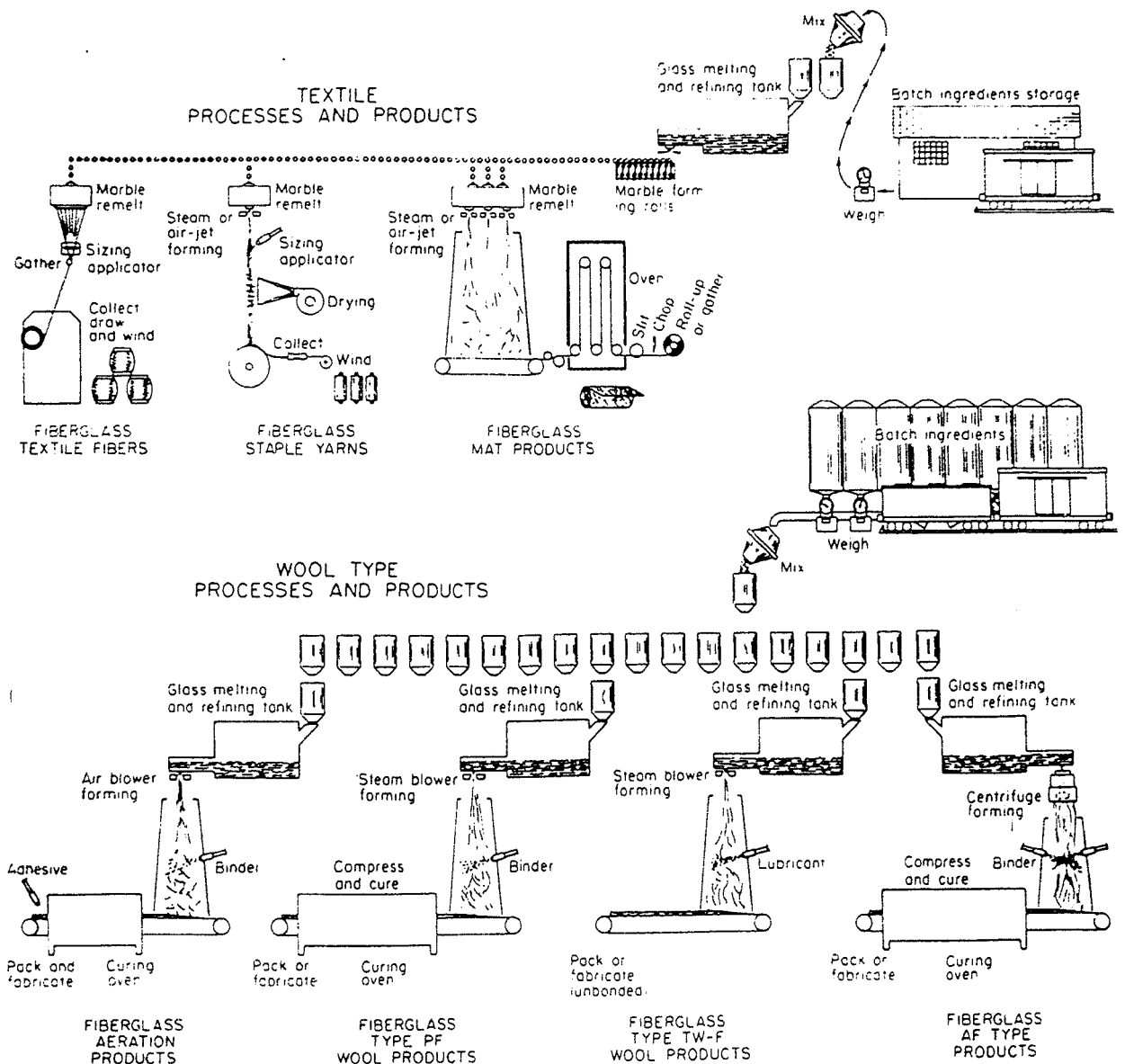


Fig. 35.6. Flowchart for Fiberglass production. (Owens-Corning Fiberglas Corp.)

holes (usually 102 or 204 in number) in a heated platinum bushing at the bottom of the furnace. The fibers are led through an "eye" and then gathered, lubricated, and put on high-speed winders, which rotate so much faster than the flow from the bushing that the filaments are drawn down to controlled diameters. The fibers are used for electrical insulation in motors and generators, structural reinforcement for plastics, fireproof wall coverings, and tire cords.¹⁰

In the production of staple fiber, glass is automatically fed at regular intervals to a small

¹⁰Rolston, Fiberglass Composite and Fabrication, *Chem. Eng.* 87 (2) 96 (1980); A Code to Build Trust in FRP Equipment, *Chem. Eng.* 86 (13) 78 (1979).

Table 35.3 Basic Ingredients for Continuous-Filament Glass Fiber (in percent)

Silicon dioxide	52-56	Boron oxide	8-13
Calcium oxide	16-25	Sodium and potassium oxides	0-1
Aluminum oxide	12-16	Magnesium oxide	0-6

electrically heated furnace. The molten glass discharges continuously through a spinneret. Directly below the orifice plate is a jet discharging high-pressure air or steam in such a manner as to seize the molten filaments and drag them downward, decreasing their diameter. The individual fibers are projected through the path of a lubricating spray and a drying torch onto a revolving drum. The resulting web of fibers on the drum is drawn off through guides and wound on tubes, and, after drafting and twisting to form yarns, sent to weaving and textile fabrication. A new process treats the fabrics at high temperature to relax the fibers, thereby increasing the drapability and "hand" and removing all sizing from the yarns to make them receptive to finishing materials. Coloring can be achieved by the use of resin-bonded pigments applied during finishing. End-use applications include curtains and draperies.

In the manufacture of glass wool for thermal and acoustical insulation, borosilicate glasses composed of approximately 65 and 35% fluxing oxides and borates, respectively, are melted in large regenerative furnaces. In blowing, molten glass at 1500°C flows through the small holes of a platinum alloy plate called a bushing, or from a centrifuge, at one end of a standard glass furnace. The melt streams are caught by high-speed gaseous jets and pulled out into fibers that are hurled onto a moving belt. This wooly mass is impregnated with various binders and formed into many shapes for use as insulation, or set into frames for use as air filters. Glass-fiber mats and wool have now largely superseded rock wool for insulation.

Multicomponent Fibers

Multicomponent fibers¹¹ have been prepared which possess superior properties to either component if spun alone. These fibers are prepared by spinning two or more polymeric compounds together. These compounds may be variants of the same polymer, as two different polymers of polypropylene, or two or more chemically unrelated materials, such as polyamides and polyesters. The choice of the starting materials is determined by the properties desired in the finished fiber. These properties may be better dyeability, permanent crimp, or silklike feel, etc.

CELLULOSIC FIBERS

Rayon and Acetate

USES AND ECONOMICS. In 1981 the U.S. production of rayon and acetate was as shown in Fig. 35.1 and amounted to 349,000 t. High tenacity viscose yarn is used mainly in cords for tires, hose, and belting. The difference in strength between ordinary and high tenacity viscose depends on the amount of orientation¹² imparted to the fiber molecules when they are made. The hydroxyl groups in the cellulose molecules enable the fiber to absorb water, resulting in low wet strength. Hydroxyl groups also serve as sites for hydrogen bonding, and thus in the dry state, serve to hold molecules together despite strong bending, resulting in fibers which tend to maintain their dry strength well even at high temperatures. The price of rayon and

¹¹Placek, *Multicomponent Fibers*, Noyes, Park Ridge, N.J., 1971.

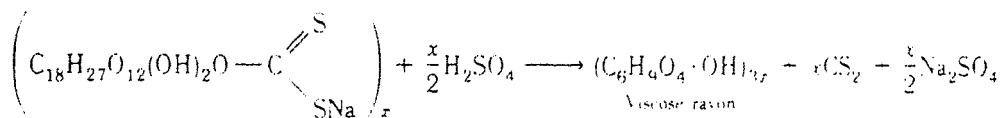
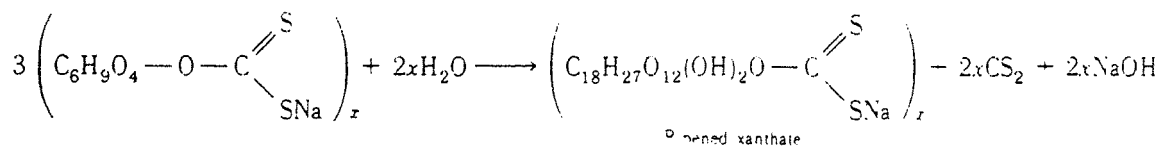
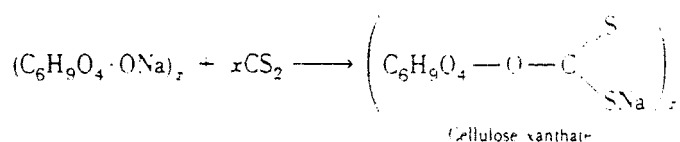
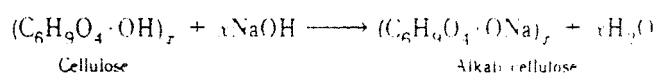
¹²Molecules lined up in one direction by stretching during spinning and drawing.

acetate varies according to the size of the filaments, process of manufacture, and type of finish. Textile rayon and acetate are used primarily in women's apparel, draperies, upholstery, and blends with wool in carpets and rugs. In 1981 cotton, wool, and silk accounted for 55 percent of the fibers produced worldwide. It has been predicted that by 1985 new, improved rayons will take over a large part of cotton's market because of increases in the price of cotton, shift of land devoted to growing cotton to growing food, and, in the United States, the large expenditures that mill owners must make to comply with the stringent government cotton dust regulations.

RAW MATERIALS. The viscose process is based on sulfite, and a little sulfate wood pulp. If sheet cellulose, the form used in viscose manufacture, is desired, the sulfate pulp, after the bleaching treatment has been completed, is blended with several other batches, passed successively through a beater and a refiner (see manufacture of pulp for paper in Chap. 33), and formed into sheets on a Fourdrinier.¹³ Viscose rayon is a major consumer of sulfuric acid, caustic soda, and carbon disulfide. Titanium dioxide is added to deluster the yarn. Cellulose acetate employs large quantities of acetic anhydride, glacial acetic acid, sulfuric acid, and acetone to swell the wood pulp. In addition to this important consumption of basic chemicals, the fiber industry needs significant quantities of dyes and other chemicals.

The viscose process produces filaments of regenerated cellulose, and the acetate forms a thread that is a definite chemical compound of cellulose, cellulose acetate. Although each of these processes is quite different as far as details of procedure are concerned, they all follow the same general outline: solution of the cellulose through a chemical reaction, ageing or ripening of the solution (peculiar to viscose), filtration and removal of air, spinning of the fiber, combining the filaments into yarn, purifying the yarn (not necessary for acetate), and finishing (bleaching, washing, oiling, and drying).

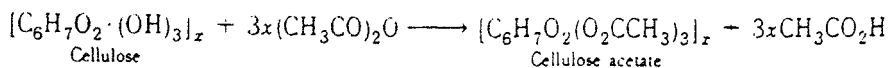
REACTIONS¹⁴



¹³*Chem. Week* 129 (5) 25 (1981); *Textile Ind.* 146 (6) 60 (1982); Layman, Rayon Aims for Specialty Niches in Low-Growth Market, *Chem. Eng. News* 61 (8) 10 (1983).

¹⁴The cellulose molecule is composed of a large, undetermined number of glucose units, here represented as $(\text{C}_6\text{H}_9\text{O}_4\text{OH})_x$. The value of x does not remain constant throughout these reactions. Each reaction causes a reduction in the molecular weight of the cellulose molecule, so that the viscose-rayon molecule is considerably smaller than the cellulose originally fed in. Some CS_2 breaks away from the cellulose xanthate during the ripening process.

Cellulose acetate



VISCOSE MANUFACTURING.¹⁵ The finished filament is pure cellulose, as shown by the equations, but, because it consists of smaller molecules than the cellulose of the original wood pulp or cotton, it possesses different physical properties.

The process as shown in Fig. 35.7 can be broken down into the following sequences:

The cellulosic raw material (sheets made from sulfite or sulfate pulp) is charged to a steeping press containing vertical perforated steel plates and is steeped either batchwise or continuously in a caustic soda solution (17 to 20%) for about 1 h at 13 to 17°C to dissolve the cellulose.

The excess liquor is drained off, removing impurities such as cellulose degradation products. The soft sheets of alkali cellulose are reduced to small crumbs in a shredder. This requires 2 to 3 h, and the temperature is maintained at 18 to 20°C.

¹⁵ECT, 3d ed., vol. 19, 1982, p. 855; Chapman, op. cit.

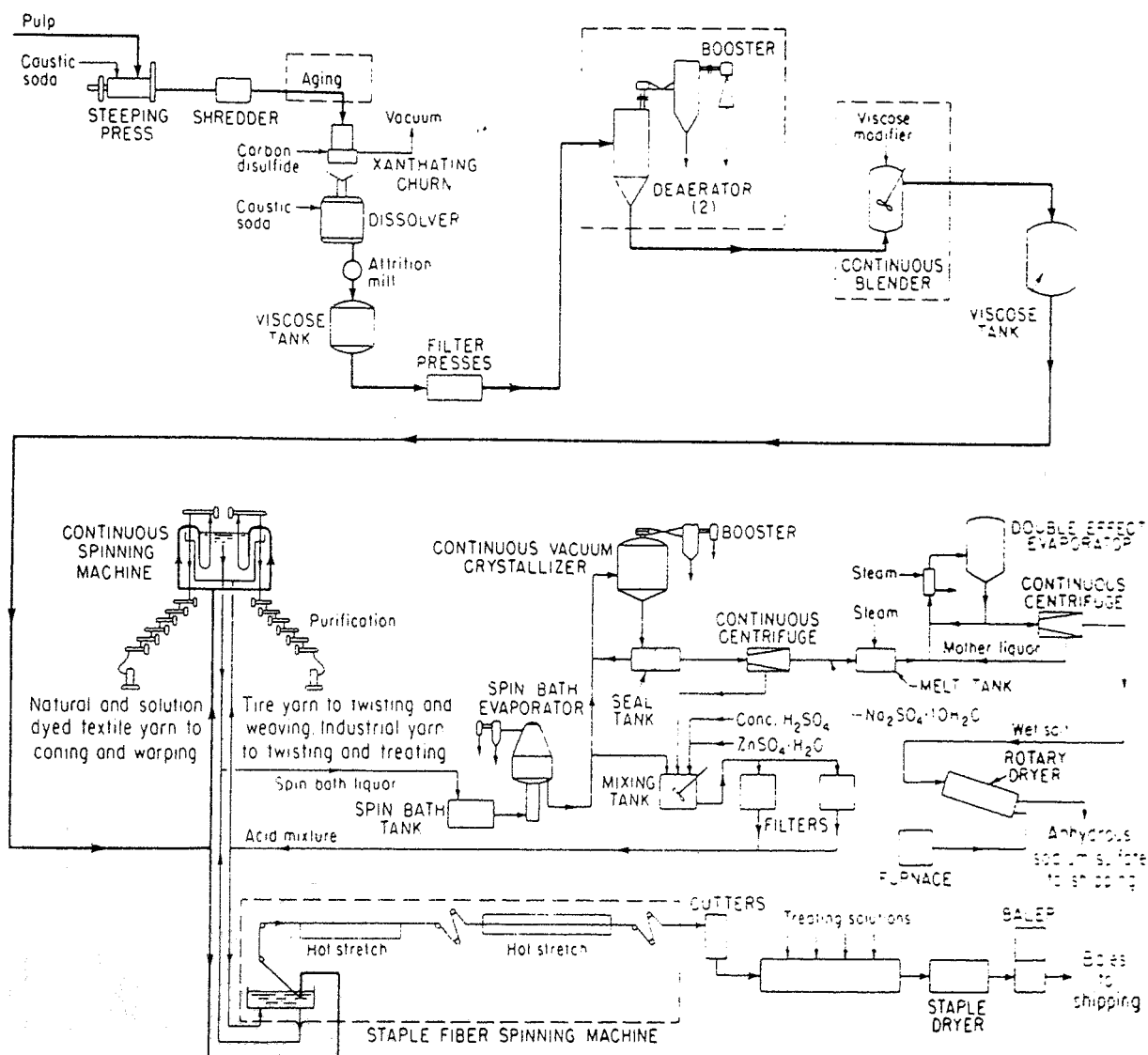


Fig. 35.7. Flowchart for viscose rayon production. [Chem. Eng. 71 (14) 110 (1964)]

The crumbs of alkali cellulose are aged either batchwise or continuously for 24 to 48 h at 24°C in large steel cans. Some oxidation and degradation occur, although the actual chemical change is unknown. Physically, correct aging produces a solution of suitable viscosity for spinning after xanthation.

The aged crumbs are dropped into large, cylindrical xanthating churns. Carbon disulfide weighing between 30 to 40% of the dry recoverable cellulose is slowly added under carefully controlled temperature and reduced pressure during 2 h of churning, during which time the crumbs gradually turn yellow and finally deep orange, and coagulate into small balls.

Still in batch form, the cellulose xanthate balls are dropped into a jacketed dissolver (vis-solver) containing dilute sodium hydroxide. The xanthate particles dissolve in the caustic, and the final product, viscose solution, contains 6 to 8% cellulose xanthate and 6 to 7% sodium hydroxide. This reaction takes 2 to 3 h. If desired, delustering agents, such as titanium dioxide or organic pigments, are added to the viscose solution in the mixer. The result is a viscous, golden-brown liquid. The remainder of the process (Fig. 35.7) through ripening and spinning is continuous. DuPont has developed a continuous belt xanthation process¹⁶ that is claimed to cut costs and produce a higher quality product. The vessel used is completely enclosed which cuts carbon disulfide losses.

During the ripening the proportion of combined sulfur decreases and the ease of coagulation increases. Thirty years ago, this conversion took 4 to 5 days, but now improved technology has reduced it to about 24 h. In a series of tanks (only one is shown in Fig. 35.7) the reaction proceeds under deaeration and continuous blending with modifiers (viscose additives, mainly amines and ethylene oxide polymers) that control neutralization and regeneration rates.

Finally, in two continuous vacuum-flash boiling deaerators (at high vacuum and below room temperature), small air bubbles are removed that would either weaken the final yarn or cause breaks during spinning.

In spinning, viscose is forced by gear pumps through thimble-like spinnerets of noble metal, each with from 750 to 2000 holes. The fine streams thus formed are injected into the spin bath where they coagulate and the cellulose is regenerated to form fiber. Sulfuric acid in the

¹⁶How to Make Viscose Rayon Continuously, *Chem. Week.* **129** (5) 25 (1981)

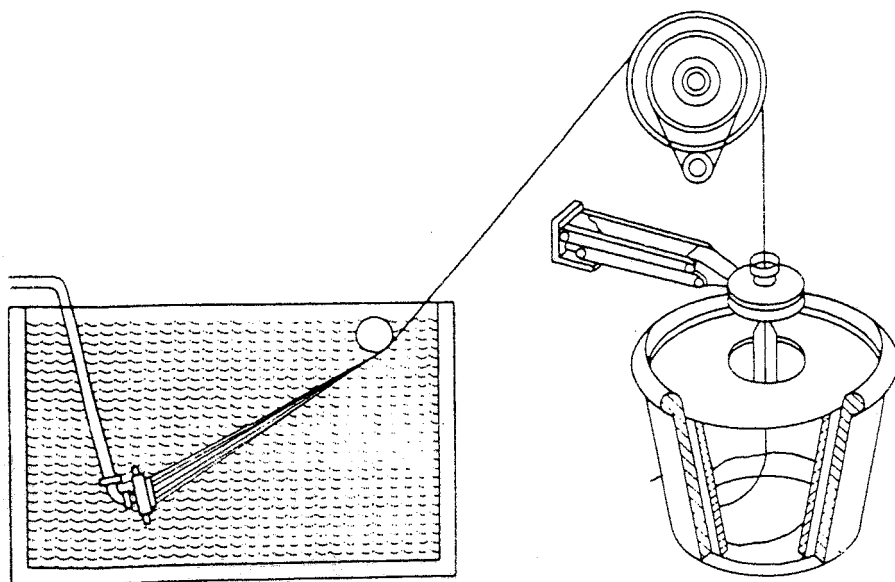


Fig. 35.8. Spinning in the viscose process.